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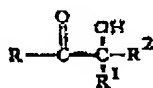
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## APPLICATION OF CARBONYL COMPOUNDS IN THE PROCESS OF TANNING HIDES

The present invention describes the application of carbonyl compounds in the process of tanning hides.

- 5 Specially, this invention describes the application of hydroxy ketones in the process of tanning hides.

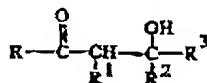
The selected  $\alpha$ -hydroxy ketonic compounds present a general formula as (I)



(I)

- 10 where R may be a linear or ramified alkyl group or even aromatic group and  $\text{R}^1$  and  $\text{R}^2$  may be hydrogen, linear or ramified alkyl or even aromatic, as, for example,  $\text{R}^1 = \text{R}^2 = \text{H}$  and  $\text{R} = -\text{CH}_2\text{CH}_3$  or, preferentially,  $\text{R}^1 = \text{R}^2 = \text{H}$  and  $\text{R} = -\text{CH}_3$ .

The selected  $\beta$ -hydroxy ketonic compounds present a general formula as (II):



(II)

- 15 where R may be a linear or ramified alkyl group or even aromatic group and  $\text{R}^1$ ;  $\text{R}^2$  and  $\text{R}^3$  may be hydrogen, linear or ramified alkyl or even aromatic, as, for example, R,  $\text{R}^1$  and  $\text{R}^2 = -\text{CH}_3$  and  $\text{R}^3 = \text{H}$ , or, preferentially, R,  $\text{R}^2$  and  $\text{R}^3 = -\text{CH}_3$  and  $\text{R}^1 = \text{H}$ .

- 20 Still in this invention, the referred carbonyl compounds may be used in an aqueous solution, in concentrations varying from 0.1% till its pure state, that is, 100%, or yet in mixtures with other organic compounds that act as diluents.

The hide is composed of proteins, lipids, glycidex, mineral salts, water etc...; collagen is the most important protein, from the point of view of the tanner (Reference: A. White and collaborators, "Principles of Biochemistry", 5<sup>th</sup> Ed., p.140).

- 25 Collagen reacts with tanning agents, originating leather; therefore, the tanning process is one of the essential operations in the process of producing leather.

Tanning, through a phenomenon of reticulation, inherent to the agent used, transforms the hide into a stable and non-putrescible material.

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To produce leathers that resist the retraction test, traditional processes use 2% to 2.5% of chrome oxide ( $\text{Cr}_2\text{O}_3$ ); generally, the leather will be tanned when about 3.5% of  $\text{Cr}_2\text{O}_3$  are incorporated into the hide.

Chrome salts adequate for normally tanning are the chrome (III) salts, as, for example, chrome (III) sulfate or basic chrome (III) sulfate [ $\text{Cr}(\text{OH})\text{SO}_4$ ; 33% basicity in Schrelemmer degrees] (Reference: E. Hoinacki, "Hides and Leathers", 2<sup>nd</sup> Edition, 1989) containing 25% to 26% of  $\text{Cr}_2\text{O}_3$ .

In the traditional processes, only 70% to 80% of chrome oxide available in the tanning bath is used.

Therefore, in traditional processes, in the bath used for chrome tanning, a residue of chrome oxide is left, with a large impact on the environment, requiring great effort on the part of the tanning companies, to treat the effluents.

For example, the 20% to 30% of the unabsorbed chrome oxide leaves a chrome residue in the tanning bath that may reach 1% (10 g of  $\text{Cr}_2\text{O}_3$ /liter of bath).

The chrome (III) compounds are not damaging to plants and animals, specially in neutral conditions, where they are insoluble, but international standards have imposed low limits for chrome (III) and other heavy metals in water and air. (Reference: Ullmann's Encyclopedia of Industrial Chemistry, Vol. A15, p. 269).

In this aspect, efforts have been made attempting to lower the residual chrome in the tanning baths, by the change in process conditions or by the use of auxiliary chemical products, not only due to ecological and environmental aspects but also for economy in the use of chemical reagents.

As is amply described in literature, the increase in pH or temperature of the tanning bath above the values used in traditional processes results in a better usage of the chrome bath.

However, the increase in pH or temperature of the bath causes a larger astringency of the chrome tanning agent, resulting in the production of leathers of inferior quality, as compared to that obtained in traditional processes, besides of lower yield and loss of area.

The use of auxiliary chemical products, with the aim of increasing absorption of chrome from the bath has also been amply described in literature.

For example, it is described in the American patent U.S.P. 4,042,321 a process of

chrome tanning with a higher chrome absorption from the tanning bath, where the hide is pre-tanned with chrome (III) salts, after pickling.

After the pre-tanning, the hide is tanned with a mixture of chrome (III) salt, binding acid agents, as for example, dolomite, magnesium oxide and carbonate or bicarbonate of alkaline and alkaline ferrous metals and di- and tricarboxylic aromatic acids, as for example, phthalic, isophthalic, succinic and similar acids, and their salts or anhydrides.

In the American patent U.S.P. 4,715,861, it is described that a higher absorption of chrome, from the tanning bath, is reached when the hides, after the pickling stage, are pre-treated, before tanning, with compounds of the carboxylic acid-aldehyde type or carboxylic acid-ketone type, such as pyruvic aldehyde, pyruvic acid and glyoxylic acid and then tanned.

A better absorption of the chrome from the tanning bath is also described in the American patent U.S.P. 4,978,361, where the hides are pre-treated before tanning, by the addition of carboxylic acid-aldehyde or acid-ketone compounds in the pickling bath itself, as for example, glyoxylic acid and tanned in the conventional manner with a mixture of chrome (III) salt, acid binding agents and di- or tricarboxylic aromatic acids.

These processes, in spite of presenting a better usage of the chrome from the tanning bath, do not eliminate the pickling stage; it is necessary to raise the tanning bath pH, increasing its basicity for the fixation of the chrome in the hide.

In the present invention, the pre-treatment of the hides with the described carboxylic compounds, preferentially hydroxy ketones and, still better,  $\beta$ -hydroxy ketones, that present advantages, if compared to the carboxylic acid-aldehyde compounds and carboxylic acid-ketone compounds since, besides propitiating a higher absorption of the chrome from the bath, its also dispense the previous use of the pickling stage.

The recycling of the tanning bath, as exemplified in the American patent U.S.P. 4,042,321 has been suggested as a way to increase the absorption of the chrome salts, diminishing the treatment of effluents. However, this process of recycling the bath is complicated, due to the large accumulation of salt and fiber residues.

According to the present invention, the pre-treatment of the hides with the carbonyl compounds (I) and (II) described, besides of propitiating a higher absorption of the chrome from the bath, dispense the previous use of the pickling stage. In this manner,

the tanning bath, by not containing salt, can be recycled after simple elimination of the fibers, through filtration.

The step of basification in the chrome tanning process can cause stains in the leather, in the case of quick additions of the basifying agent or larger doses than  
5 necessary; it is, therefore, always a problematic stage, that should be made with care and attention.

The hides, after deliming, bating and the pre-treatment with the carbonyl compounds (I) and (II) described in this invention, propitiate a higher absorption of the chrome from the bath, dispense the previous use of the pickling stage and the  
10 addition of the chrome salt can be made at a pH in the range of 4 to 6. After the normal chrome tanning time, the pH of the bath ends up at the range of 3.8 to 4.1; no correction of basicity is needed.

A larger exhaustion of the chrome bath is also described in the European patents EP 0 822 263 and Brazilian patents PI 96.3419-0 A and PI 9702025-7 A, by the use  
15 of a water solution of stabilized aldehydes, more specifically, 3-hydroxyl butanal (aldol).

DE-A-402 545 discloses a process for tanning hides in which aldehydes are used.

However, aldehydes in general are extremely toxic and have a small limit of  
20 exposition, as for example, 2-hydroxyl butanal (aldol), whose LD<sub>50</sub> is 2180 mg/kg (mice, oral) (Reference: H.E. Christensen, Toxic Substances, Edition 1974, p.166).

Aldol, particularly, frequently contains crotonaldehyde as an impurity (2-butenal), which is lacrimator, extremely irritant to the eyes (Reference: Merck Index 9<sup>th</sup> Edition, p. 338), with an extremely low exposition: TLV-TWA = 2 mg/kg  
25 (Reference: Compendium of Safety Data Sheets for Research and Industrial Chemicals, p. 427).

The aldol characteristics described previously make this product extremely difficult to be handled in the tanning plants. Besides this, the hides treated with aldol acquire an intense and suffocating residual odor.

30 The present invention describes the application of carbonyl compounds, such as hydroxy ketones and, preferentially,  $\beta$ -hydroxy ketones, where the hides, before the chrome tanning process or tanning process, with or without pickling, are pre-treated with the carbonyl product, at 0.1% to 30%, preferentially 0.5% to 10% and, better still, 1% to 5% of weight, in relation to the weight of the hides.

35 The hides, pre-treated with the carbonyl compounds of general structure (I) and (II), are prepared for the process to produce the "Wet Blue" leathers, and may also be

pre-treated by the process described in this invention to be used for the "Wet White" manufacturing process or for vegetal tanning with tannins, aiming the manufacture of sole leather.

The carbonyl compounds used in this invention are preferentially  $\beta$ -hydroxy ketones, added into the water tanning bath itself, in their pure form or in mixture with inert compounds, preferentially pure or in a water solution. The subsequent chrome tanning treatment is made in the traditional manner, using the commercially available chrome (III) salts, such as basic chrome sulfate; the pre-treatment using the carbonyl compounds, described in this invention permits a larger absorption of the chrome, with a consequent diminishing of residual chrome in the bath.

In the classic tanning process, the hides are previously submitted to a pickling bath with a pH = 2.5 to 3.0 and the tanning bath having, for example, the following bath weight/hide weight composition: 70% to 100% water, 2% to 5% sodium chloride (salt) and 2.5% to 3.0% chrome (III) oxide.

Under the conditions of low pH, the affinity of the chrome salts for the protein, collagen, is minimal, and so the penetration of the tanning agent occurs.

After penetration of the chrome into the hide, the gradual elevation of the pH (for ex., 3.8 to 4.0) provokes a reaction between the proteins and the chrome salts.

The carbonyl compounds described in this invention react with the free amino groups of the polypeptidic chain of the collagen.

In function of this reaction, the new bond formed in the polypeptidic chain alters the isoelectric point, pH where there is no migration of a dipolar ion when submitted to an electric field, to values lower than the isoelectric point of the collagen.

This new isoelectric point of the polypeptidic chain permits a greater ionization of the carboxyls at a higher pH, allowing a higher reactivity and penetration of the chrome salts into the hide.

Due to this property, the hides after the steps of deliming and bating, can be pre-treated with the carbonyl compounds described in this invention and are prepared for tanning with chrome salts or tannin, with the complete elimination of pickling, the basification step and with a larger exhaustion of the chrome bath; the residual chrome in the process of this invention can reach levels as low as 0.02% to 0.05% of chrome.

In addition to the environmental impacts occasioned by the larger exhaustion of

the chrome bath when treating the hides with the carbonyl products described in this invention, the elimination of the pickling step still permits a large reduction of the polluting load coming from the residues of sulfuric acid and the sodium chloride used in the pickling stage.

5 As a consequence, the application of the carbonyl products described in this invention for the tanning hides reduces the use of chemical inputs and reduces the tanning processing time, consequently giving a gain in productivity.

The carbonyl compounds of general structure (I) and (II) described in this invention, preferentially  $\alpha$ -hydroxy ketones and more preferentially,  $\beta$ -hydroxy ketones, 10 besides of reacting with the amino groups of the collagen, as described previously, confer an additional advantage, since the hydroxyl groups are capable of bonding to determined groups of the polypeptidic chain by hydrogen bond.

This property, one of the characteristics of the tannins, is described as the probable mechanism operating in the vegetal tanning process, with tannin (Reference: E. 15 Hoinacki, "Hides and Leathers", 2<sup>nd</sup> Edition, 1989).

The petitioner discovered that the use of carbonyl products in the hide tanning process described in this invention, preferentially hydroxy ketones and even better,  $\beta$ -hydroxy ketones, presents large advantages when compared to the use of the water solution of stabilized aldehydes, more specifically, 3-hydroxyl butanal (aldol), since they 20 are easy to handle, having, in general, a pleasant odor and not leaving a residual odor in the hides, after pre-tanning and tanning with chrome or tannin.

The process, according to this invention, can be illustrated by the examples below, where all the products are added in percentages in product weight/hide weight, except if otherwise specified. The examples below are merely illustrative, and should not 25 be taken as a limitation of the invention.

#### EXAMPLE 1

The hides, divided to 3-4 mm (37 kg) are first washed at the temperature of 35°C to 37°C for 20 minutes, in a tanning drum containing 200% of water and 0.2% of ammonium sulfate, based on the weight of the hides. The drum is drained and the hides are delimed 30 for 2 hours, adding 1.7% of ammonium sulfate, 0.5% of a non-swelling organic acid and 1% of sodium bisulfite. Add 0.15% of a commercial proteolytic enzyme (for ex.: "Lipose 5"). At the end of these operations, the cross section of the hides is colorless to

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phenolphthalein. Add 0.2% of an anionic tensoactive agent and 0.3% of formic acid. Run the drum for 1 hour. After this time, the bath has a pH = 5 and the cross section of the hide a pH = 5 to 7. Add 0.1% of formic acid, run the drum for 40 minutes, drain the bath and wash the hides 3 times for 10 minutes, with water at ambient temperature. At the end of this operation, the pH of the cross section of the hide is around 5.5. Add 40% of water, 0.2% of formic acid, 3% of the carbonyl compound, diacetone alcohol and run for 2 hours. Add 6% of a commercial chrome salt, in two portions, for example, basic chrome sulfate with 33% basicity and 25% to 26% chrome oxide (III) and run for 13 hours. The final temperature of the bath is 40°C to 42°C and the final pH is 3.8 to 4.0.

- 10 After the procedure of usual finishing, the leathers obtained are soft, presenting a smooth and fine surface and uniform dyeing.

#### EXAMPLE 2

- The hides, divided into 36 kg lots, are washed for 20 minutes in a tanning drum containing 200% of water and 0.2% of ammonium sulfate. Drain the bath, add 0.3% of a tensoactive agent (for ex.: "Pardon Green"), 1.5% of ammonium sulfate, 0.5% of an organic acid, 1% of sodium bisulfate and run for 1 hour. At the end of this time, the pH of the bath is around 7.5 to 8 and the cross section of the hide does not still turn red, with phenolphthalein. Add 0.05% of "Lipose S" and run for 10 minutes (bath pH = 7 to 7.5 and the cross section of the hide has a pH of 7.0). Add 0.5% of formic acid, run for 30 minutes, drain the bath and wash the hides 3 times for 10 minutes with water at ambient temperature. Add 50% of water, 3% of the carbonyl compound, diacetone alcohol, (bath pH = 5.5 to 5.7) and run for 2 hours. Add 6% of basic chrome sulfate with 33% basicity and 25% to 26% of chrome oxide (III), in two portions and run for 13 hours. The final temperature of the bath is in the range of 40°C, pH = 3.8 to 4.0 and the residual bath contains 0.04% of chromium.

#### EXAMPLE 3

- The hides, divided into 36 kg lots, are washed for 20 minutes in a tanning drum containing 200% of water and 0.2% of ammonium sulfate. Drain the bath, add 0.3% of a tensoactive agent (for ex.: "Pardon Green"), 1.5% of ammonium sulfate, 0.5% of formic acid, 1% of sodium bisulfate and run for 1 hour. At the end of this time, the pH of the bath is around 7.5 to 8 and the cross section of the hide is colorless to phenolphthalein. Add 0.05% of "Lipose S" and run for 10 minutes (pH of the bath = 7 to 7.5 and the pH of the cross section of the hide = 7.0). Add 0.5% of formic acid, run for 30 minutes, drain

the bath and wash the hides 3 times for 10 minutes, with water at ambient temperature. Add 50% of water, 2% of the carbonyl compound, diacetone alcohol (bath pH = 5.5 to 6.0) and run for 2 hours. Add 4% of basic chrome sulfate with 33% basicity and 25% to 26% of chrome oxide (III), in two portions and run for 15 hours. The final temperature of the bath is in the range of 38°C to 40°C, pH = 4.0 to 4.4 and the residual bath contains 0.026% of chrome

#### EXAMPLE 4

The hides, divided into 26 kg lots, are washed for 20 minutes in a tanning drum containing 200% of water and 0.2% of ammonium sulfate. Drain the bath, add 0.3% of a tensoactive agent (for ex.: "Pardon Green"), 1.5% of ammonium sulfate, 0.5% of formic acid, 1% of sodium bisulfate and run for 1 hour. At the end of this time, the pH of the bath is around 7.5 to 8 and the cross section of the hide does not turn red, with phenolphthalein. Add 0.05% of "Lipose S" and run for 10 minutes (pH of the bath = 7 to 7.5 and the pH of the cross section of the hide = 7.0). Add 0.45% of formic acid, run for 30 minutes, drain the bath and wash the hides 3 times for 10 minutes with water at ambient temperature. Add 50% of water, 0.1% of formic acid, 2% of the carbonyl compound, diacetone alcohol (bath pH = 4.0 to 4.2) and run for 2 hours. Add 4% of basic chrome sulfate with 33% basicity and 25% to 26% of chrome oxide (III), in two portions and run for 13 hours. The final temperature of the bath is in the range of 38°C to 40°C, pH = 4.0 to 4.2 and the residual bath contains 0.04% of chrome.

#### EXAMPLE 5

One thousand seven hundred kg (1700 kg) of hide divided, are placed into a tanning drum and washed for 20 minutes with 200% of water and 0.2% of ammonium sulfate. Drain the bath, add 1.5% of ammonium sulfate, 0.2% of a tensoactive agent (for ex.: "Eusapon S"), 0.5% of formic acid, diluted 1:5 and 1% of sodium bisulfate. Run for 30 minutes. At the end of this time, the pH of the bath is around 7.4 to 7.5 and the cross section of the hide is colorless to phenolphthalein. Add 0.06% of "batan 100" and run for 30 minutes. Add 0.5% of formic acid diluted 1:5 and run for 2 hours. After this time, the pH of the bath and of the cross section of the hide = 5 to 5.5. Drain the bath and wash the hides 3 times for 10 minutes, with water at ambient temperature.

Add 40% of water, 0.1% of formic acid and run for 30 minutes (pH of the bath = 4.3 to 4.5). Add 2% of the carbonyl compound, diacetone alcohol and run for 2 hours (initial bath pH = 4.5 and pH = 5, at the end). Add 4.5% of basic chrome sulfate with



33% basicity and 25% to 26% of chrome oxide (III), in two portions, and run for 8 hours. After this time, heat the bath to 45°C. Add 0.1% of a bactericide (for ex.: "Busan 30") and 0.3% of sodium formate and run for 5 hours. The final pH of the bath is in the range of 3.8 to 4 and the residual bath contains 0.08% of chrome.

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#### EXAMPLE 6

Two thousand five hundred kg (2500 kg) of laminated, integral 'gruons', are placed into a tanning drum and washed for 20 minutes with 200% of water, 0.2% of ammonium sulfate and 0.05% of "ultrader S100". Drain the bath, add 2% of ammonium sulfate, run for 10 minutes, add 2% of ammonium sulfate, run for 10 minutes, add 2% of sodium bisulfate, run for 10 minutes, add 0.5% of an organic acid (for ex.: "Kalplex MK"), diluted 1:5, 0.2% of "ultrader S100", 0.03% of a bacterial purge, run for 30 minutes. At the end of this time, the pH of the bath is around 7.0 to 7.2 and the cross section of the hide is colorless to phenolphthalein. Add 0.3% of formic acid diluted 1:5 and run for 1 hour. Add 0.1% of formic acid diluted 1:5 and run for 1 hour. After this time, the pH of the bath = 5.5 and of the cross section of the hide = 5.5 to 6.0. Drain the bath and wash the hides 3 times for 10 minutes, with water at ambient temperature. Add 40% of water, 3% of the carbonyl compound, diacetone alcohol and run for 15 hours (initial bath pH = 5.7 to 5.8 and final pH = 5). After the pre-treatment with the carbonyl products described in this invention, the hides are prepared for the normal vegetal tanning sequence with tannins, to manufacture sole leather.

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#### EXAMPLE 7

One thousand nine hundred kg (1900 kg) of 'gruons' are placed into a tanning drum and washed for 15 minutes with 150% of water and 0.2% of ammonium sulfate. Drain the bath, add 20% of water, 2% of ammonium sulfate, 1.2% of sodium bisulfate, 0.1% of "eusapon", 0.6% of "interox" and run for 2 hours.

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At the end of this time, the pH of the bath is around 7.0 to 7.2 and the cross section of the hide is colorless to phenolphthalein. Add 0.03% of bacterial purge, run for 40 minutes and drain. Add 0.5% of formic acid diluted 1:5 and run for 2 hours (bath pH = 5.4 to 5.5). Wash the hides twice for 10 minutes, with 150% of water at ambient temperature. Add 20% of water, 0.15% of formic acid and run for 30 minutes (bath pH = 4.1 to 4.2). Add 2% of the carbonyl compound, diacetone alcohol and run for 2 hours (initial bath pH = 4.2 to 4.3 and final pH = 4.7 to 4.8). Add 2.5% of a synthetic

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commercial tannin, 0.01% of a bactericide and run for 3 hours. After the pre-treatment, with the carbonyl products described in this invention, the hides are prepared for the normal vegetal tanning sequence with tannins, to manufacture sole leather.

#### EXAMPLE 8

5 One thousand nine hundred kg (1900 kg) of 'gruons' are placed into a tanning drum and washed for 15 minutes with 150% of water and 0.2% of ammonium sulfate at a temperature of 35°C. Drain the bath, add 20% of water, 2% of ammonium sulfate, 1.2% of sodium bisulfate, 0.1% of "eusapon", 0.6% of "interox" and run for 2 hours. At the end of this time, the pH of the bath is around 7.0 to 7.2 and the cross section of the hide is colorless to phenolphthalein. Add 0.03% of a bacterial purge, run for 40 minutes and drain. Add 0.5% of formic acid diluted 1:5 and run for 2 hours (bath pH = 5.4 to 5.5). Wash the hides twice for 10 minutes, with 150% of water at ambient temperature. Add 20% of water, 0.15% of formic acid and run for 30 minutes (bath pH = 4.1 to 4.2). Add 2% of the carbonyl compound, diacetone alcohol and run for 2 hours (initial bath pH = 4.2 to 4.3 and final pH = 4.7 to 4.8). Add 2.5% of a synthetic commercial tannin, 0.01% of a bactericide and run for 3 hours (final bath pH = 4.9 to 5.0). After the pre-treatment with the carbonyl products described in this invention, the hides are prepared for the normal vegetal tanning sequence with tannins, to manufacture sole leather.

#### EXAMPLE 9

20 One thousand eight hundred kg (1800 kg) of 'gruons' are placed into a tanning drum and washed for 20 minutes with 150% of water and 0.2% of ammonium sulfate at a temperature of 35°C. Drain the bath, add 20% of water, 2% of ammonium sulfate, 1% of sodium bisulfate, 0.1% of "eusapon", 0.6% of "interox" and run for 2 hours. At the end of this time, the pH of the bath is around 7.0 to 7.2 and the cross section of the hide is colorless to phenolphthalein. Add 0.03% of a bacterial purge, run for 40 minutes and drain. Add 0.8% of formic acid diluted 1:5 and run for 2 hours (bath pH = 4.7 to 4.8). Wash the hides twice for 15 minutes, with 150% of water at ambient temperature. Add 20% of water, 0.35% of formic acid and run for 30 minutes (bath pH = 4.1 to 4.2). Add 2% of the carbonyl compound, diacetone alcohol and run for 2 hours (initial bath pH = 4.2 to 4.3 and final pH = 4.5 to 4.6). Add 3% of a synthetic commercial tannin, 0.03% of a bactericide and run for 3 hours (final bath pH = 4.8 to 4.9).